

Summary
Charleston Sanitary Board Request for Cooper WER
WVDEP - Water Quality Standards Program, June 2014

WV WQS

West Virginia state law requires that all changes to state water quality standards, as outlined in 47CSR2 *Requirements Governing Water Quality Standards*, must be approved by state legislature prior to being submitted for final approval by EPA. This requirement for review and approval includes any site-specific changes including Water Effect Ratio (WER) requests.

What is a Copper Water Effect Ratio (WER)?

A WER measures the ratio of toxicity in specific "site water" in comparison to the toxicity in standard laboratory water for certain metals. WER calculations develop site-specific limits for certain metals from EPA and/or state adopted aquatic life criteria that were originally developed using laboratory toxicity data. The water effect ratio incorporates site-specific factors that can influence the bioavailability and toxicity of metals. A WER is typically applied to a specific discharger but, if adequate sampling is completed, can be applied to specific reaches or portions of a waterbody. EPA originally developed and published WER protocols in 1994 and later revised the protocols in 2001, and published the "Streamlined Water-Effect Ratio Procedure for Discharges of Copper" document (EPA-822-R-01-005).

CSB Request – Summary of Events

The Charleston Sanitary Board (CSB) met with WVDEP in September, 2013 to initiate the discussion of a potential copper WER effort. WVDEP discussed options, including the potential use of the EPA approved BLM method and CSB decided to move forward with the WER approach. CSB provided a WER sampling plan that was reviewed by both WVDEP and EPA (and revised the final plan based on the review comments and recommendations). A copy of the final WER sampling plan has been attached to this summary which includes a map of the plant discharge location and the location of the upstream sampling point. The WER testing was conducted on samples collected during sampling events on October 15, 2013 and November 18, 2013. Results for both events were forwarded on to WVDEP for review, and WVDEP shared both results with EPA staff for review. Both WVDEP and EPA provided comments and questions to CSB (and the contract lab).

WER Sampling/Laboratory Results

The EPA guidance document states that stream flow should be stable during sampling events and that water quality conditions should be compatible with those occurring during periods when nonpoint source inputs of organic matter and suspended solids are relatively low. There were no significant precipitation events immediately prior to the collection of the first sample and the flow rate in the Kanawha River remained stable and near baseflow conditions. The effluent flow rate recorded by CSB on the day of the first sampling event (October 15, 2013) was 7.72 MGD. The average effluent flow for the month of October was 7.95 MGD.

The effluent flow rate recorded by CSB on the day of the second sampling event (November 18, 2013) was 10.3 MGD. A precipitation event occurred the day before the second sampling event in which the plant recorded 0.18 inches of rainfall which CSB did not consider to be significant. CSB submitted photographic documentation to WVDEP showing sample and river water clarity at the time of the second sampling event, and the flow rate in the Kanawha River remained stable and near baseflow conditions. The photographs show typical appearance of surface water during low runoff conditions. The average effluent flow rate for the month of November was 9.18 MGD.

WVDEP requested sampling data to evaluate plant performance during both sampling events and a spread sheet containing these data has been attached. The information presented by CSB and reviewed by WVDEP was consistent with the requirements of the Streamlined Water-Effect Ratio Procedure for Discharges of Copper EPA guidance document.

R.E.I Consultants conducted the WER toxicity testing for copper for CSB in accordance with the Streamlined Procedure guidance document. Both WVDEP and EPA reviewed the laboratory results and, as outlined above, provided comments and questions to the contract lab. The contract lab addressed all comments and questions and revised reports as necessary. Based on the two sampling events, the calculated site WER based on SMAV EC50s is 5.62.

CSB Water Effects Ratio (WER)

Summary Documents/Attachments:

- WER Study plan & photos of WWTP location and sampling points
- River and rainfall reports - WER sampling events #1 and #2
- Photos - River conditions and clarity WER #2
- CSB WWTP plant performance data
- Summary lab reports - WER #1 and WER #2
- CSB/DEP correspondence (DEP/EPA WER review)

CSB Water Effects Ratio (WER)

- WER Study plan & photos of WWTP location and sampling points



October 11, 2013 (REV1)

PROPOSED WATER-EFFECT RATIO (WER) FOR COPPER

1. Objective

The Sanitary Board of the City of Charleston, WV (hereinafter called “CSB”) is conducting the WER to develop a site-specific numeric criterion for copper for the Charleston Wastewater Treatment Plant Outlet WV0023205-001 (hereinafter called “001”). The WER will be based on the guidance provided in the USEPA’s (EPA) “Streamlined Water-Effect Ratio Procedure for Discharges of Copper” (EPA 822-R-01-005, March 2001) [hereinafter called “EPA Guidance”].

2. Approach

- 2.1. CSB’s Environmental Compliance Staff will collect samples at the following (2) two locations:
(a.) A 24-hour composite at 001 and (b.) Composited core sample approximately 203-feet upstream of 001, in the Kanawha River.
- 2.2. Creating the simulated downstream sample (“site-sample”): The 001 sample will be mixed with the upstream sample at the dilution corresponding to the design low-flow condition that the permitting authority (DEP) uses in its permit limit calculations. DEP confirmed to use 33.5% effluent to 66.5% upstream sample to create the site-sample. The site-sample will then be spiked with various concentrations of copper sulfate 5-hydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$). A side-by-side sample of laboratory-water will be spiked with the copper sulfate 5-hydrate at the same various concentrations. Acute toxicity testing using *Ceriodaphnia Dubia* will be performed in the copper spiked site-sample and laboratory-water sample to obtain the 48-hour EC50.

2.3. A site specific WER will be the geometric mean of the two sample WERs derived from site-sample EC50 divided by the laboratory-water EC50.

3. Parameters

3.1. The parameters to be analyzed for this study (at 001 and upstream samples) are:

Table 3.1 – Parameters, Methods, MDL, PQL, Containers, Preservation and Hold Times

Parameter	Method	MDL (mg/L)	PQL (mg/L)	Container Type	Container Size	Preservative	Max. Hold Time
Copper, Total Recoverable	E200.8	0.001	0.005	Polyethylene	500-mL	Cool to 4°C; HNO3 to pH<2	6-months
Copper, Dissolved	E200.8	0.001	0.005	Polyethylene	500-mL	Field Filtered, then Cool to 4°C; HNO3 to pH<2	6-months
Hardness	SM2340 B	NA	1	Polyethylene	500-mL	Cool to 4°C; HNO3 to pH<2	6-months
Upstream pH	CSB Field Meter	NA	NA	Polyethylene	250-mL	None	Instant
**001 and Lab pH	SM4500H-B	NA	NA	Polyethylene	250-mL	None	Instant
Alkalinity	SM2320 B	1	10	Polyethylene	250-mL	Cool to 4° C	14-days
Dissolved Organic Carbon	SM5310 C Modified	0.2	1	Amber Glass	250-mL	Field Filtered, then Cool to 4°C; H2SO4 to pH<2	28-days
Total Suspended Solids	SM2540 D	2	10	Polyethylene	1000-mL	Cool to 4° C	7-days

3.2 Research Environmental and Industrial Consultants, Inc. (REIC) [DEP Lab Certification No. 060] was selected as a contract laboratory for the purpose of this study. REIC will analyze the following parameters: Copper, Total Recoverable; Copper, Dissolved; Hardness; pH (at various times as part of the acute toxicity testing); Alkalinity; Dissolved Organic Carbon and Total Suspended Solids. Because the pH needs to be read within 15-mins, CSB personnel will use its portable pH meter for the upstream sample pH. **CSB lab will run pH (method SM4500H-B) in the lab on a grab sample the morning the 001 composite comes off and REIC labs will be using this same pH method during the acute toxicity testing part of the WER.

3.3 REIC will be performing a 48-hour acute toxicity test using *Ceriodaphnia dubia* for EC50 (as discussed in part 2.2 above), following the EPA's Acute Toxicity Testing Manual EPA-821-R-02-012.

4. Sampling Stations

4.1. Sampling Locations¹

- 4.1.1. At 001: A Sigma 900 portable sampler will be used to collect a 24 hour composite sample at the WWTP Outlet (Lat 38° 22' 19" N Long 81° 40' 42" W).
- 4.1.2. At Upstream of 001: Approximately 203-feet upstream of 001 (Lat 38° 22.227'N Long 81° 40.682'W), which is outside the influence of the discharge at 001, and away from non-point source discharges. A core sampler (aka, Sludge Judge) will be used to retrieve a composite core from the water surface to approximately three-quarters of the depth to the river bottom.

5. Sampling Schedule

- 5.1.1. Samples will be collected during stable flow conditions in the Kanawha, during time periods when nonpoint source inputs are relatively low (during dry weather).
- 5.1.2. Two sampling events shall occur, the first in October and the second in November, weather permitting.

6. QA requirements

- 6.1.1. Sample collection and equipment shall be in accordance with Method 1669 Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels, July 1996, using "Clean Hands Dirty Hands" techniques.
- 6.1.2. A Field Blank using distilled water supplied by Tyler Mountain Water will be conducted at each sample site (001 and upstream river sample). The sample will be preserved with Nitric Acid and analyzed for Total Recoverable Copper.
- 6.1.3. A core sampler will be used to collect the Kanawha River sample. Each core sample will be deposited into a 2.5-gallon, food grade baggy then poured off into a 5-gallon sample cube. Alternatively, depending upon the sample cube REIC provides CSB, the core samples may be poured off directly into the 5-gallon sample cube. After thoroughly mixing the sample cube, pH will be read and aliquots for total recoverable copper, dissolved copper, TSS, alkalinity, Hardness and dissolved organic carbon will be poured off into labeled containers (with the required preservative, as called out in Table 3.1). A sigma 900 Sampler will be utilized to draw sample from the 5-gallon sample cube, through an in-line Enviro-Tech Disposable Capsule Filter (0.45-µm), into sample bottles for the dissolved copper and dissolved organic carbon samples.
Prior to field sampling, an Equipment Blank will be collected in the lab by filling the core sampler with distilled water and using a Sigma 900 Sampler to pump the water through an in-line Enviro-Tech Disposable Capsule Filter (0.45-µm). The sample will be preserved with Nitric Acid and analyzed for the Total Recoverable and Dissolved forms of Copper and Dissolved Organic Carbon.

¹ Attachment No. 1 shows the WER Sample Locations

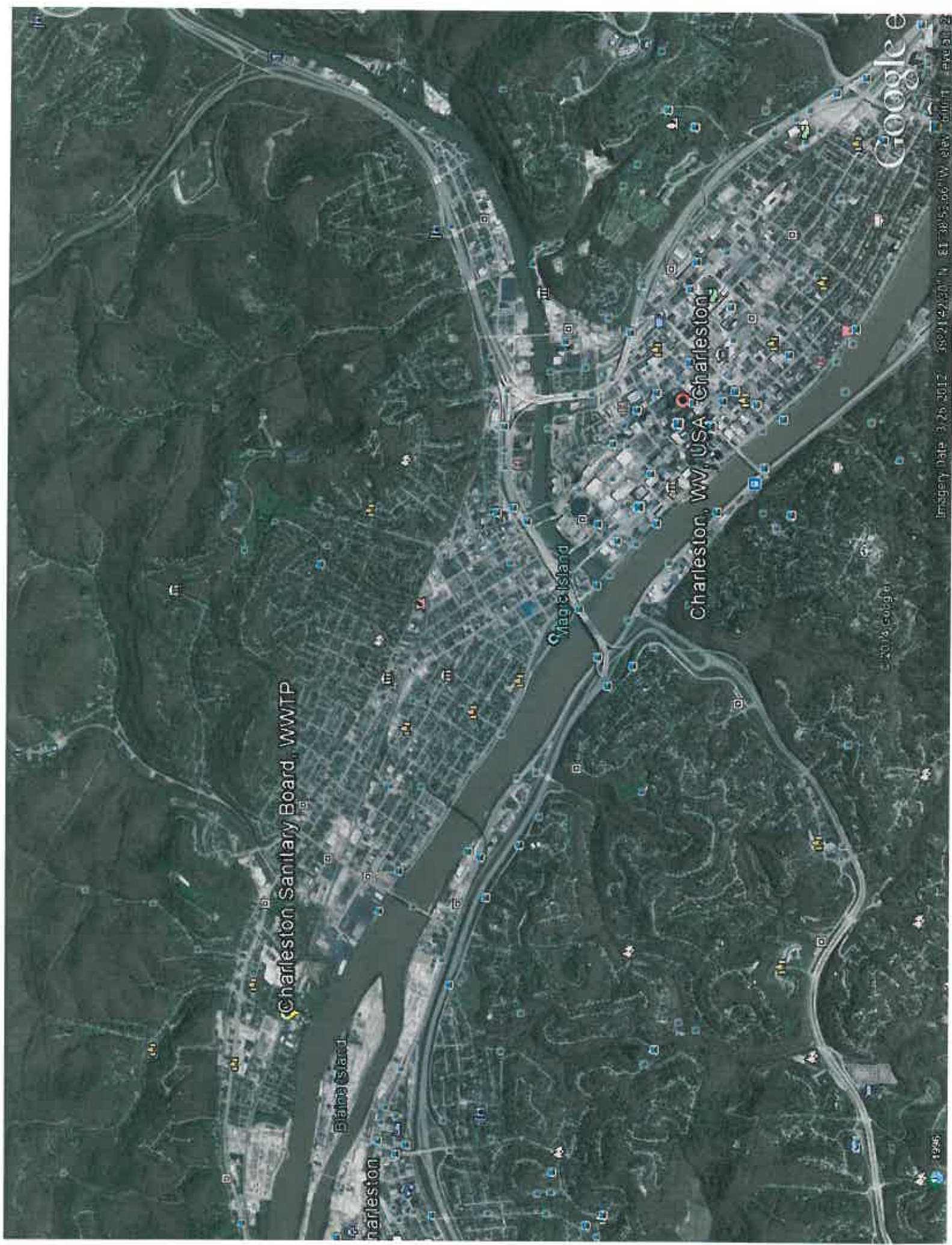
- 6.1.4. Enough sample volume will be properly preserved and only analyzed when a data set appear to be questionable.
- 6.1.5. Samples will be properly labeled, immediately iced and have chain-of-custody forms.
- 6.1.6. CSB has a pontoon boat that it will utilize to collect its river samples. Barge traffic will be noted to ensure sampling does not occur after a barge passes the sample area.
- 6.1.7. The 001 composite sample will be poured off into individual sample bottles (with the required preservative, as indicated in Table 3.1) for the parameters listed in Table 3.1. A one gallon cube will also be filled with the composited 001 sample for use by REIC in setting up the test solutions.

7. Testing, calculating and reporting the WER

- 7.1 Testing, calculating and reporting the WER will be in accordance with Appendix A of the EPA Guidance.
- 7.2 The method for preparing the test solutions for the test chambers shall be as follows: Prepare a large volume of simulated downstream water by mixing effluent and upstream water in the desired ratio; place the same known volume of the simulated downstream water in each test chamber; add the necessary amount of copper, which will be different for each treatment; and mix thoroughly and let stand for 1 to 4 hours.
- 7.3 The laboratory-water EC50 and site-water EC50 will be normalized to the same hardness using the formula:

$$\text{EC50 at Std Hdns} = \text{EC50 at Sample Hdns} * \{\text{Std Hdns}/\text{Sample Hdns}\}^{0.9422}.$$

- 7.4 Each sample shall be calculated by $\text{WER} = \text{site-sample EC50} / \text{laboratory-water EC50}$. The site specific WER will be the geometric mean of the two sample WERs.



Charleston Sanitary Board, WWTP

Blaine Island

Charleston

Magic Island

Charleston, WV, USA Charleston

Google

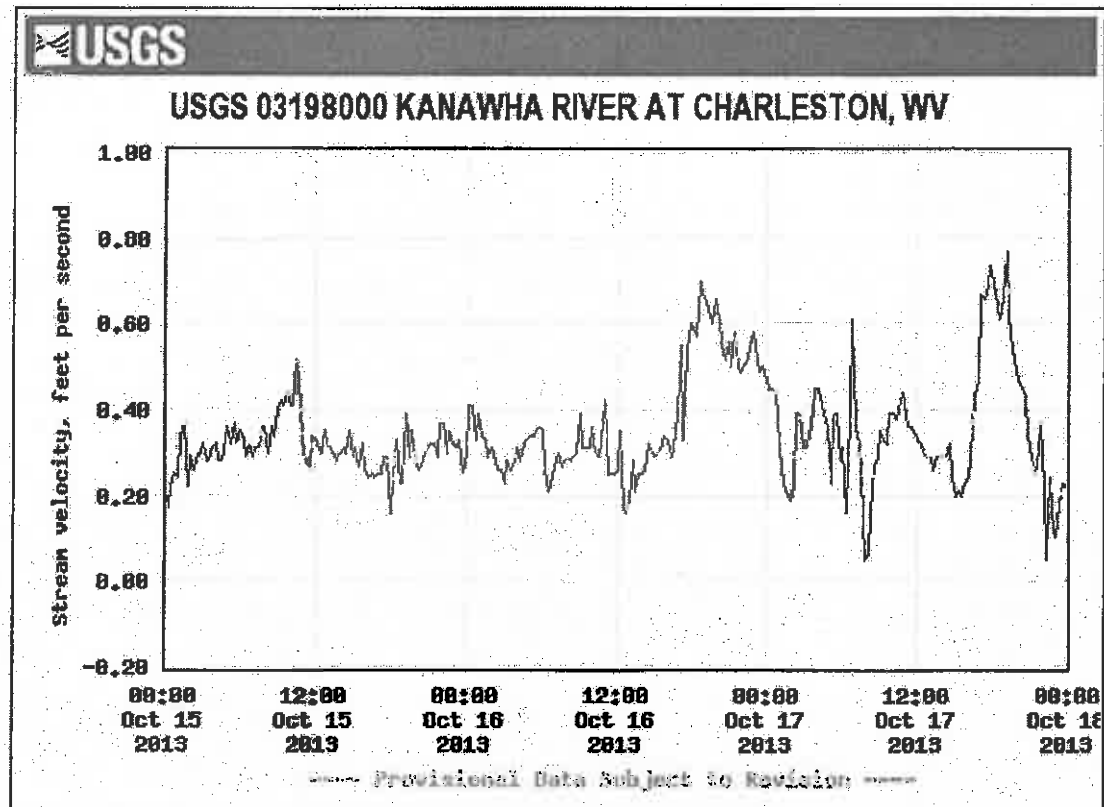
Imagery Date: 3/26/2017 38°21'42.20"N 81°38'53.96"W View: 600m 30° 2'

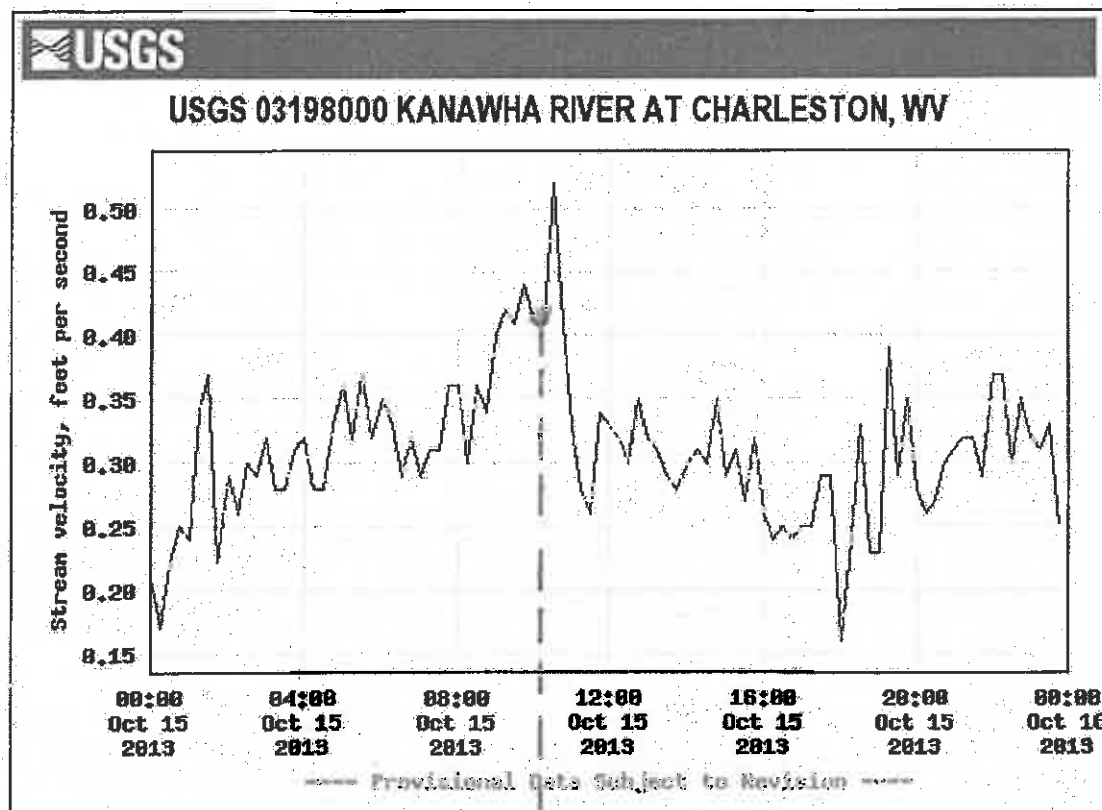
- Legend**
- Sample Point
 - Outlet Location

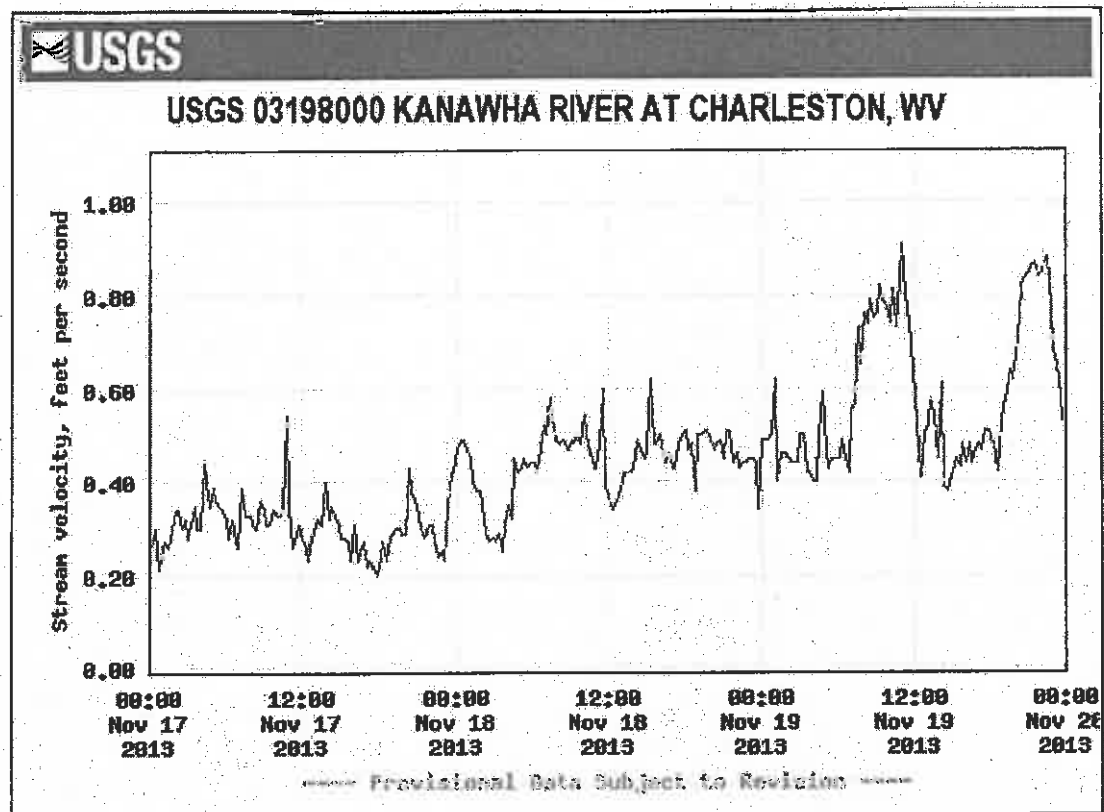


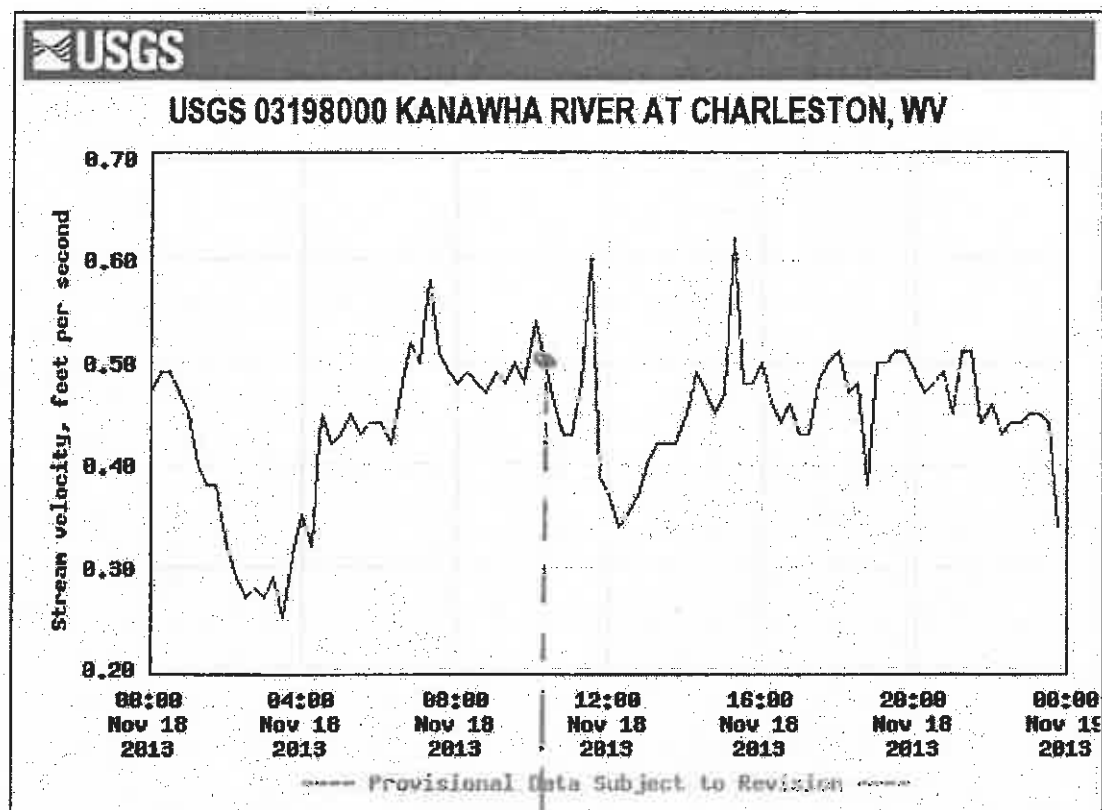
CSB Water Effects Ratio (WER)

- River and rainfall reports - WER sampling events #1 and #2









WER# 2

CSD RIVER SAMPLES
TAKEN 11-18-13 FROM

10:13 - 10:25 AM

CSB's TREATMENT PLANT RAIN GAGE SUMMARY

Date	Time	Peak (in/hr)	Total (in)	Duration (hrs)
10/07/13	2:10	0.07	0.28	6:20:00
10/16/13	15:10	0.04	0.18	25:00:00
10/22/13	7:00	0.07	0.30	33:00:00
10/30/13	4:30	0.10	0.26	4:20:00
10/31/13	14:50	0.09	0.14	14:50:00
11/07/13	2:10	0.12	0.48	6:50:00
11/12/13	3:00	0.05	0.21	9:10:00
11/15/13	19:50	0.04	0.09	4:40:00
11/17/13	14:30	0.08	0.18	8:40:00
11/22/13	6:50	0.07	0.12	8:00:00

CSB Water Effects Ratio (WER)

- Photos - River conditions and clarity WER #2



Receiving stream,
upstream of Outlet No.
001. Note, stable flow
conditions, no nonpoint
source interference and
good water clarity.



Core sample underway
in receiving stream,
upstream of Outlet No.
001. Note the good
clarity in the receiving
stream.



Note...good clarity of river water in sample cube.



Note...good clarity of river water in core sampler.

CSB Water Effects Ratio (WER)

- CSB WWTP plant performance data

NPDES MONTHLY WORKSHEET

MONTH OF October, 2013

DATE	EFF.FLOW	pH		BOD ₅				SUSPENDED SOLIDS				AMMONIA NITROGEN				EFF. FECAL COLIFORM		
				INF.		EFF.		INF.		EFF.		INF.		EFF.		log10	COLONIES/100 ml	ln
		INF.	EFF.	mg/l	lbs.	mg/l	lbs.	mg/l	lbs.	mg/l	lbs.	mg/l	lbs.	mg/l	lbs.			
1	8.07	7	7	170	11000	8.9	800	160	11000	8.8	590	17	1100	14	940	0.89897 *	5	1.6094379
2	8.2	7	7	180	12000	11	760	200	14000	12	820					1.25627 *	18	2.8903718
3	7.79	7	7	190	12000	12	780	170	11000	8.5	550	18	1200	15	970	1.17609 *	15	2.7080502
4	7.47	7	7	210	13000	12	750	180	11000	8.5	530	18	1100	18	1100			
5	7.97																	
6	7.64			7-day averages		11	720			9.4	620							
7	7.52	7	6									15	940	9.8	610	1.80206	40	3.6888795
8	10.4	7	7	180	18000	10	870	280	24000	9.8	830	12	1000	11	950	1.23045 *	17	2.8332133
9	9.08	7	7	160	12000	9	680	260	20000	9.5	720					1.63347	43	3.7612001
10	7.54	7	7	200	12000	10	630	140	8800	11	690	19	1200	15	940	1.77815	60	4.0943448
11	7.8	7	7	220	14000	11	720	210	14000	14	910	19	1200	20	1300			
12	7.66																	
13	7.26			7-day averages		10	720			11	790							
14	7.21	7	7	7-day avg Percent Limits		30	875			45	780	18	1100	12	720	1.88124	48	3.871201
15	7.72	7	7	200	13000	10	640	200	13000	9	580	18	1200	17	1100	1.74819	56	4.0253517
16	7.92	7	7	200	13000	11	730	210	14000	18	1000		1200			2.39794	250	5.5214609
Avg	7.95	7				10	720			11	720			15	960		33	
Percent Limits:				6 to 6		20	3500			30	6750			15	2000	400 max (avg) 200 max (avg) means		

Percent Removals: Act. 95% Limit 95%

Act. 95% Limit 95%

NPDES MONTHLY WORKSHEET

MONTH OF: November, 2013

DATE	EFF.FLOW	pH		BOD ₅				SUSPENDED SOLIDS				AMMONIA NITROGEN				EFF. FECAL COLIFORM		
				INF.		EFF.		INF.		EFF.		INF.		EFF.				
		INF	EFF.	mg/l	lbs.	mg/l	lbs.	mg/l	lbs.	mg/l	lbs.	mg/l	lbs.	mg/l	lbs.	log10	COLONIES/100 ml	In
1	9.9	7	7	200	16000	9	740	210	17000	5.2	430	16	1300	16	1300			
2	10.5											15	1300					
3	7.87											16	1000					
4	7.5	7	6									17	1100	12	750	1.38021 *	24	3.1780538
5	7.92	7	6	170	11000	8.8	580	190	12000	6	400	18	1200	19	1200	1.30103 *	20	2.9957323
6	7.9	7	6	190	12000	7.9	520	170	11000	9.5	620	19	1200			1.44718 *	28	3.3322045
7	9.08	7	7	260	20000	11	830	290	22000	8.8	670	15	1100	18	1200	1.00000 *	10	2.3025851
				7-day averages:		9.2	670			7.4	530							
				7-day avg Permit Limit:		30	3250			45	2861							
8	12.1	7	7	130	13000	9.8	990	180	18000	10	1000	9.3	940	12	1200			
9	8.82																	
10	8.19																	
11	7.4	7	6									16	990	12	740	1.07918 *	12	2.4849068
12	9.01	7	7	180	14000	5.7	430	200	15000	12	900	16	1200	17	1300	0.72428 *	5.3	1.6677068
13	11.2	7	6	210	20000	7.5	700	190	18000	6	560	12	1100			1.43136	27	3.2958369
14	8.77	7	7	180	13000	5.1	370	130	9500	4	290	17	1200	16	1200	1.04139 *	11	2.3978953
				7-day averages:		7	620			8	680							
15	8.64	7	6	200	14000	6.3	450	170	12000	2.9	210	18	1300	19	1400			
16	8.88											16	1200					
17	8.23											18	1100					
18	12.2	7	6									10	1000	11	1100	1.07918 *	12	2.4849068
19	10.3	7	7	140	12000	5.6	480	110	9500	5.5	470	15	1300	12	1000	0.82607 *	6.7	1.9021075
Avg	9.18					7.7	610			7	560			15	1100		14	
Permit Limits:				30		3250		45		2861		12		2862		4000 max day/200 min day/1000		

CSB Water Effects Ratio (WER)

- Summary lab reports - WER #1 and WER #2
- CSB/DEP correspondence (DEP/EPA WER review)



RESEARCH ENVIRONMENTAL & INDUSTRIAL CONSULTANTS, INC.

Post Office Box 286 • Beaver, WV 25813 • 800.999.0105

304.255.2500 • 304.255.2572(fax)

website: www.reiclabs.com

Improving the environment, one client at a time...

COPPER STREAMLINED
WATER EFFECT RATIO TOXICITY TEST
ON SAMPLES COLLECTED 10-16-13

Conducted For:

Charleston Sanitary Board
208 26th Street
Charleston WV 25387
Attn: Mr. Tim Haapala

By:

R. E. I. Consultants, Inc.
225 Industrial Park Road
Beaver West Virginia 25813

Ed J. Kirk, Director - Biological Division
Mike Lester, Bioassay Lab Manager
Mike Hofe, Environmental Monitoring Manager

October 31, 2013

2013 OCT 31 PM 4:02



RESEARCH ENVIRONMENTAL & INDUSTRIAL CONSULTANTS, INC.

Post Office Box 286 • Beaver, WV 25813 • 800.999.0105

304.255.2500 • 304.255.2572(fax)

website: www.reiclabs.com

Improving the environment, one client at a time...

Copper Streamlined Water Effect Ratio Toxicity Test

Executive Summary

The Streamlined Water Effects Ratio ("WER") Dilute Mineral Water toxicity test is incorporated into the full WER suite of tests as an indicator of the baseline toxicity of the target component (copper in the case of South Charleston Sanitary Board). The toxicity of the copper within the dilute mineral water test is then compared to the toxicity of copper within the site water test as a measure of the amount of buffering capacity the site water has on the target component.

The WER Dilute Mineral Water toxicity test consisted of nine (9) spiked test concentrations (13.0, 16.7, 21.6, 27.9, 36.0, 46.5, 60.0, 77.5, and 100.0 $\mu\text{g/L}$ copper) and a Control, which contained no added copper. The test was prepared by measuring out 1 liter of dilute mineral water into each of the ten 1-liter test beakers. The nine test concentrations were then each spiked with a 0.100 g/L copper sulfate ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$) stock solution (TABLE 1). Each of the nine test concentrations was then mixed after the addition of the copper sulfate aliquots, and was allowed to set for two (2) hours prior to loading of the test organisms.

The organism-loaded test beakers were checked at 24-hours and all test organisms had died in all spiked test concentrations. All test organisms survived in the Control. Therefore, a second test was initiated utilizing lower test concentrations of copper sulfate. This second set of concentrations consisted of 1.0, 3.0, 6.0, 9.0, and 12.0 $\mu\text{g/L}$ and a second (new) Control. This second test was prepared in the same manner as the first trial, but with the above listed lower concentrations of copper sulfate.

This test was performed for 48 hours, and was checked for mortality and or effects at 24 hours as well as at the end of the 48-Hr test, and a trimmed Spearman-Kärber statistical test was incorporated on the final survival data to calculate the EC50 for the Dilute Mineral Water test.

There were no mortalities (0%) in the Control Dilute Mineral Water test concentration; no mortalities (0%) in the 1.0 and 3.0 $\mu\text{g/L}$ test concentrations; 40% mortality in the 6.0 $\mu\text{g/L}$ test concentration; and 100% mortality in the 9.0 and 12.0 $\mu\text{g/L}$ copper sulfate test concentrations.

Because the actual copper concentrations within the test dilutions will differ slightly from the targeted hypothetical copper test concentrations, aliquots of the spiked dilutions were analyzed post-test to determine the actual concentrations of total copper. For instance, the targeted 6.0 $\mu\text{g/L}$ copper test concentration was measured to actually contain copper concentrations of 6.5, 6.6 and 6.4 $\mu\text{g/L}$ copper, and thus a mean of 6.5 $\mu\text{g/L}$ was utilized within the statistical methods to calculate the EC50. Aliquots of the Control and dilutions were analyzed at 0, 24, and 48-Hours in order to determine if copper concentrations decreased during the test. Means of these values were then utilized within the statistical analyses to calculate the EC50 using the "true" concentrations of copper rather than the targeted hypothetical concentrations.

Using these actual, analytically-derived, copper concentrations, the resulting EC50 for the Dilute Mineral Water toxicity test was calculated to be 6.24 $\mu\text{g/L}$ total copper.

The Streamlined Water Effects Ratio ("WER") Site Water toxicity test is incorporated into the full WER suite of tests as an indicator of the buffering capacity of the receiving stream for the target component (copper in the case of Charleston Sanitary Board). The toxicity of the copper within the dilute mineral water test is then compared to the toxicity of copper within the site water test as a measure of the amount of buffering capacity the site water has on the target component.

The WER Site Water toxicity test was initiated by warming both the collected full-strength effluent and the collected upstream river water sample to 25°C. The river water sample was then filtered through a 60-micron screen to remove debris, potential organisms, and algae. The Site Water test consisted of nine (9) spiked test concentrations (13.0, 16.7, 21.6, 27.9, 36.0, 46.5, 60.0, 77.5, and 100.0 µg/L copper) and a River Water Control, which contained no added copper. As directed by the WV-DEP, the test was prepared by combining 335 milliliters of 100% effluent with 665 milliliters of Upstream River Water into a glass flask and mixing the solution well. Each of the nine test concentrations were then spiked with a 0.100 g/L copper sulfate ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$) stock solution (TABLE 1). Each of the nine test concentrations was then mixed after the addition of the copper sulfate aliquots, and was allowed to set for two (2) hours prior to loading of the test organisms.

The organism-loaded test beakers were checked at 24-hours and no test organisms had died in any of the spiked test concentrations. Therefore, a second test was initiated utilizing higher (stronger) test concentrations of copper sulfate. This second set of concentrations consisted of 200.0, 300.0, 400.0, 500.0, and 600.0 µg/L and a second (new) River Water Control. This second test was prepared in the same manner as the first trial, but with the above listed higher concentrations of copper sulfate.

This test was performed for 24 hours, since all test organisms were dead except for the River Water Control. There were no mortalities (0%) in the River Water Control test concentration, and 100% mortality in the 200.0, 300.0, 400.0, 500.0, and 600.0 µg/L copper sulfate test concentrations. The "graphical" method was incorporated on the final survival data to calculate the EC50 for the Site Water test.

Because the actual copper concentrations within the test dilutions will differ slightly from the targeted hypothetical copper test concentrations, aliquots of the spiked dilutions were analyzed post-test to determine the actual concentrations of total copper. For instance, the targeted 100.0 µg/L copper test concentration of the Site Water test was measured to actually contain copper concentrations of 89.6, 102.0, and 99.4 µg/L copper, and thus a mean of 97.0 µg/L was utilized within the statistical methods to calculate the EC50. Aliquots of the Upstream River Water Control and Site Water dilutions were analyzed at 0, 24, and 48-Hours in order to determine if copper concentrations decreased during the test. Means of these values were then utilized within the statistical analyses to calculate the EC50 using the "true" concentrations of copper rather than the targeted hypothetical concentrations.

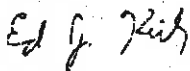
Using these actual, analytically-derived, copper concentrations, the resulting EC50 for the Upstream Site Water toxicity test was calculated to be 130.3 µg/L total copper.

Because the EC50 for the Dilute Mineral Water toxicity test was calculated to be 6.24 µg/L total copper compared to the EC50 for the Upstream Site Water toxicity test of 130.3 µg/L total copper, the receiving stream, the Kanawha River, has a tremendous buffering capacity for copper.

The measured hardness of the Dilute Mineral Water was 82.9 mg/L. The measured average hardness of the Site Water was 89.2 mg/L. Utilizing the formula provided in the Streamlined Water-Effect Ration Procedure Guidance, the Dilute Mineral Water EC50 of 6.24 µg/L and Site Water EC50 of 130.3 µg/L were normalized to a hardness of 100 mg/L. The normalized Dilute Mineral Water EC50 was calculated to be 7.45 µg/L total copper. The normalized Site Water EC50 was calculated to be 145.2 µg/L total copper.

The WER based on the normalized Dilute Mineral Water EC50 calculates as 19.5 (145.2/7.45). If the *Ceriodaphnia dubia* Species Mean Acute Value (SMAV) EC50 of 24 µg/L is used the WER calculates as 6.05 (145.2/24).

Sincerely,

A handwritten signature in black ink, appearing to read "Ed J. Kirk". The signature is written in a cursive, slightly slanted style.

Ed J. Kirk
Director - Biological Division
R.E.I. Consultants, Inc.
304-255-2500 Beckley, WV Office
540-570-3149 Cell
ekirk@reiclabs.com

**STREAMLINED WATER EFFECT RATIO "WER"
TOXICITY TEST FOR COPPER CONDUCTED FOR
CHARLESTON SANITARY BOARD**

SUBMITTED TO:

**CHARLESTON SANITARY BOARD
208 26TH STREET
CHARLESTON WV 25387
ATTN: MR. TIM HAAPALA**

By:

**R. E. I. CONSULTANTS, INCORPORATED
225 INDUSTRIAL PARK ROAD
BEAVER WV 25813**

**ED J. KIRK, DIRECTOR - BIOLOGICAL DIVISION
MIKE LESTER, MANAGER - BIOASSAY LABORATORY
MIKE HOFE, PROJECT ENGINEER**

December 11, 2013



RESEARCH ENVIRONMENTAL & INDUSTRIAL CONSULTANTS, INC.

Post Office Box 286 • Beaver, WV 25813 • 800.999.0105

304.255.2500 • 304.255.2572(fax)

website: www.reiclabs.com

Improving the environment, one client at a time...

Copper Streamlined Water Effect Ratio Toxicity Test

Executive Summary

The Streamlined Water Effects Ratio ("WER") Dilute Mineral Water toxicity test is incorporated into the full WER suite of tests as an indicator of the baseline toxicity of the target component (copper in the case of Charleston Sanitary Board). The toxicity of the copper within the dilute mineral water test is then compared to the toxicity of copper within the site water test as a measure of the amount of buffering capacity the site water has on the target component.

The 2nd of two WER Dilute Mineral Water toxicity test consisted of nine (9) spiked test concentrations (4.30, 4.78, 5.31, 5.90, 6.56, 7.30, 8.10, 9.00 and 10.00 µg/L copper) and a Control, which contained no added copper. A dilution factor of 0.9, and the results of the previous (first) WER test, was utilized to compress the targeted test concentrations, and pinpoint the EC50. The test was prepared by measuring out 1 liter of dilute mineral water into each of the ten 1-liter test beakers. Then, the nine test concentrations were each spiked with a 0.100 g/L copper sulfate ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$) stock solution (TABLE 1). Each of the nine test concentrations was then mixed after the addition of the copper sulfate aliquots, and was allowed to set for two (2) hours prior to loading of the test organisms.

This test was performed for 48 hours, and was checked for mortality and or effects at 24 hours as well as at the end of the 48-Hr test, and the maximum likelihood Probit statistical test was incorporated on the final survival data to calculate the EC50 for the Dilute Mineral Water test.

There were 2 mortalities (10%) in the Dilute Mineral Water Control; 0 (0%) mortalities in the 4.30 µg/L test concentration; 1 mortality (5%) in the 4.78 µg/L; 4 mortalities (20%) in the 5.31 µg/L; 7 mortalities (35%) in the 5.90 µg/L; 8 mortalities (40%) in the 6.56 µg/L; 16 mortalities (80%) in the 7.30 µg/L; 17 mortalities (85%) in the 8.10 µg/L test concentrations; and 20 mortalities (100%) in the 9.0 µg/L and 10.0 µg/L test concentrations.

Because the actual copper concentrations within the test dilutions will differ slightly from the targeted hypothetical copper test concentrations, aliquots of the spiked dilutions were analyzed post-test to determine the actual concentrations of total copper. For instance, the targeted 6.56 µg/L copper test concentration was measured to actually contain copper concentrations of 8.1, 8.4 and 7.8 µg/L copper, and thus a mean of 8.1 µg/L was utilized within the statistical methods to calculate the EC50. Aliquots of the Control and dilutions were analyzed at 0, 24, and 48-Hours in order to determine if copper concentrations decreased during the test. Means of these values were then utilized within the statistical analyses to calculate the EC50 using the "true" concentrations of copper rather than the targeted hypothetical concentrations.

Using these actual, analytically-derived, copper concentrations, the resulting EC50 for the Dilute Mineral Water toxicity test was calculated to be 8.31 µg/L total copper.



RESEARCH ENVIRONMENTAL & INDUSTRIAL CONSULTANTS, INC.

Post Office Box 286 • Beaver, WV 25813 • 800.999.0105

304.255.2500 • 304.255.2572(fax)

website: www.reiclabs.com

Improving the environment, one client at a time...

The Streamlined Water Effects Ratio ("WER") Site Water toxicity test is incorporated into the full WER suite of tests as an indicator of the buffering capacity of the receiving stream for the target component (copper in the case of Charleston Sanitary Board). The toxicity of the copper within the dilute mineral water test is then compared to the toxicity of copper within the site water test as a measure of the amount of buffering capacity the site water has on the target component.

The WER Site Water toxicity test was initiated by warming both the collected full-strength effluent and the collected upstream river water sample to 25°C. The river water sample was then filtered through a 60-micron screen to remove debris, potential organisms, and algae. The Site Water test consisted of nine (9) spiked test concentrations (86.1, 95.7, 106.3, 111.8, 131.2, 145.8, 162.0, 180.0 and 200.0 µg/L copper) and a River Water Control, which contained no added copper. As directed by the WV-DEP, the test was prepared by combining 335 milliliters of 100% effluent with 665 milliliters of Upstream River Water into a glass flask and mixing the solution well. Each of the nine test concentrations were then spiked with a 0.100 g/L copper sulfate ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$) stock solution (TABLE 1). Each of the nine test concentrations was then mixed after the addition of the copper sulfate aliquots, and was allowed to set for two (2) hours prior to loading of the test organisms.

There were 0 mortalities (0%) in the River Water Control; 2 mortalities (10%) in the 86.1 µg/L; 7 mortalities (35%) in the 95.7 µg/L; 11 mortalities (55%) in the 106.0 µg/L; 12 mortalities (60%) in the 111.8 µg/L; 19 mortalities (95%) in the 131.2 µg/L test concentrations. All test organisms (100%) died in the 145.8 µg/L, 162.0 µg/L, 180.0 µg/L, and 200.0 µg/L test concentrations.

Because the actual copper concentrations within the test dilutions will differ slightly from the targeted hypothetical copper test concentrations, aliquots of the spiked dilutions were analyzed post-test to determine the actual concentrations of total copper. For instance, the targeted 95.7 µg/L copper test concentration of the Site Water test was measured to actually contain copper concentrations of 96.2, 87.9 and 98.5 µg/L copper, and thus a mean of 94.2 µg/L was utilized within the statistical methods to calculate the EC50. Aliquots of the Upstream River Water Control and Site Water dilutions were analyzed at 0, 24, and 48-Hours in order to determine if copper concentrations decreased during the test. Means of these values were then utilized within the statistical analyses to calculate the EC50 using the "true" concentrations of copper rather than the targeted hypothetical concentrations.

Using these actual, analytically-derived, copper concentrations, the resulting EC50 for the Upstream Site Water toxicity test was calculated to be 103.9 µg/L total copper.

Because the EC50 for the Dilute Mineral Water toxicity test was calculated to be 8.31 µg/L total copper compared to the EC50 for the Upstream Site Water toxicity test of 103.9 µg/L total copper, the receiving stream, the Kanawha River, has a tremendous buffering capacity for copper.

The measured hardness of the Dilute Mineral Water was 73.2 mg/L. The measured average hardness of the Site Water was 82.05 mg/L. Utilizing the formula provided in the Streamlined Water-Effect Ration Procedure Guidance, the Dilute Mineral Water EC50 of 8.31 µg/L and Site Water EC50 of 103.9 µg/L were normalized to a hardness of 100 mg/L. The normalized Dilute Mineral Water EC50 was calculated to be 11.15 µg/L total copper. The normalized Site Water EC50 was calculated to be 125.2 µg/L total copper.



RESEARCH ENVIRONMENTAL & INDUSTRIAL CONSULTANTS, INC.

Post Office Box 286 • Beaver, WV 25813 • 800.999.0105

304.255.2500 • 304.255.2572(fax)

website: www.reiclabs.com

Improving the environment, one client at a time...

The WER based on the normalized Dilute Mineral Water EC50 calculates as 11.2 (125.2 divided by 11.15). If the *Ceriodaphnia dubia* Species Mean Acute Value (SMAV) EC50 of 24 µg/L is used the WER calculates as 5.22 (125.2 divided by 24).

The site WER, calculated as the geometric mean of the two sampling event WERs based on Dilute Mineral Water EC50s, is 14.8. The site WER, calculated as the geometric mean of the two sampling event WERs based on SMAV EC50s, is 5.62.

Thank you for utilizing us to conduct these tests for you. Please do not hesitate to contact us should you have questions, or if we can be of further assistance.

Sincerely,

Ed J. Kirk
Director - Biological Division
R.E.I. Consultants, Inc.
304-255-2500 Beckley, WV Office
540-570-3149 Cell
ekirk@reiclabs.com



February 10, 2014

via: e-mail to Kevin.R.Coyne@wv.gov

Kevin,

CSB's responses (in red italicized text) to your 2-7-14 e-mail are as follows:

And as I said during the conversation – it would be good to start on a summary report of the WER effort that would include a summary of the sampling events (mainly the environmental conditions as the pertain to WER guidance requirements), brief summary of the WER #1 and #2 results (and just reference the lab reports in the summary for the details), and a final summary of the WER requested by CSB (essentially the final calculated number). Again, we are more than willing to work with you on this.

CSB's brief summary of WER sampling events and results:

CSB's WER for copper was based upon the guidance in the USEPA's "Streamlined Water-Effect Ratio Procedure for Discharges of Copper" (EPA 822-R-01-005, March 2001). CSB captured two sampling events at least one month apart. Regarding the "Upstream Outlet No. 001" samples, the river flow during each sampling event was stable and water quality was unaffected by recent rainfall run-off. Regarding the "Outlet No. 001" samples, CSB WWTP was performing well and BOD and TSS parameters were within NPDES Permit limitations.

The Executive Summary in the REIC reports (copies provided to DEP) for each WER sampling event provides a concise overview of the results. The details of the analytical results are provided in the successive sections of each of the REIC reports.

For WER#1: The WER is 19.5 based on the normalized dilute mineral water EC50. If the SMAV for ceriodaphnia dubia EC50 is used, the WER is 6.05.

For WER#2: The WER is 11.2 based on the normalized dilute mineral water EC50. If the SMAV for ceriodaphnia dubia EC50 is used, the WER is 5.22.

Geo. Mean: Taking the geometric mean of the results from both WERs, the WER is 14.5 based on the normalized dilute mineral water EC50. If the SMAV for ceriodaphnia dubia EC50 is used, the WER is 5.62.

WER 1

1. The CSB Chains of Custody (COCs) for outlet 001 and upstream outlet 001 composite samples collected 10-15 through 10-16-2013 does not provide the pH of the samples. The EPA Streamlined Water-Effect Ratio Procedure for Discharges of Copper requires analysis of pH. Since pH is a field parameter, the analysis should have been performed at the time of sampling and this data should have been included on the COC. Please provide this parameter and/or indicate in the report where this is located.

pHs were taken, but not written down on the CSB's COCs. The pH results were: 6.76 @ Outlet No. 001 and 7.25 @ Upstream Outlet No. 001. Attached are corrective copies of the COC for each sample.

2. The CSB COC for Upstream Outlet 001 lists a compositing duration of 10:06 10-15-13 through 10:20 10-16-13 however the COC shows that the samples were relinquished at 9:00 on 10-16-13 (which is before the end of the compositing period). Please provide clarification if this is an error on the report, COC, or an issue with the monitoring device.

The CSB's COC for Upstream Outlet No. 001 is correct as reported. The Upstream Outlet No. 001 sample was a composited grab using a core sampler (taken between 10:06 to 10:20 am on 10-15-13). The samples were cooled after collection and picked up by REIC Lab the following day, 10-16-13. See Part 6. QA Requirements, sub section 6.1.3 of the CSB's Proposed WER for Copper (10-11-13) for sampling procedure.

WER 2

3. The sample information provided in the REIC data report states that the composite sample at upstream outlet 001 was collected from 7:00 11-18-13 to 7:00 11-19-13 (*this is the "Outlet No. 001" 24-hr composite dates and times, not the "Upstream Outlet No. 001"*) however the COC for this sample states that the sample was collected from 10:13 11-18-13 to 10:25 (presumably on 11-19-13). The COC also states that the sample was relinquished on 11-19-13 at 8:05 which is not consistent with the collection time on the COC. Please provide clarification if this is an error on the report, COC, or an issue with the monitoring device.

The sample times and dates for "Upstream" Outlet No. 001 and Outlet No. 001 are interchanged in this comment.

The CSB's COC for Upstream Outlet No. 001 is correct as reported. The Upstream Outlet No. 001 sample was a composited grab using a core sampler (taken between 10:13 to 10:25 am on 11-18-13). The samples were cooled after collection and picked up by REIC Lab the following day, 11-19-13. See Part 6. QA Requirements, sub section 6.1.3 of the CSB's Proposed WER for Copper (10-11-13) for sampling procedure.

4. The CSB COC for upstream outlet 001 does not provide the temperature at which the samples were received by the laboratory. Please provide this parameter and/or indicate in the report where this is located.

The temperature reading is encircled (2°C) in the lower right corner of the CSB's COC. Upon receipt in its lab, REIC measures the temperature of the samples and records it on the CSB's COC. The temperatures that REIC measured were included on each CSB

COC, but may not have been legible in the copies sent to the DEP. Here's a summary of the sample temperatures for both WERs:

Sample Site:	Outlet No. 001	Upstream Outlet No. 1	Equipment Blanks
WER #1	1.6°C	1.6°C	1.6°C
WER#2	2.0°C	2.0°C	6.0°C

5. Method Detection Limits (MDLs) are not provided in the analytical data for equipment blanks. Please provide and/or indicate in the report where this is located – or an explanation of why this was not reported.

REIC didn't have the cell with the MDL turned on to display it in its program. Attached is a corrective copy of REIC's analytical data showing the MDL.

6. The analysis date shown for dissolved organic carbon in the laboratory data is 1-22-13. This date is not consistent with the collection date of the samples and is most likely a reporting error but please clarify to ensure this is a reporting error.

REIC confirmed that the date was incorrectly entered into its program. The correct date is 11-22-13. Attached is a corrective copy of REIC's analytical data showing the correct date.

THE SANITARY BOARD OF THE CITY OF CHARLESTON, WEST VIRGINIA



Tim G. Haapala, P.E.
CSB Operations Manager

WO#: 1311J31

Date Reported: 12/11/2013

Client:	CHARLESTON SANITARY BOARD	Collection Date:	11/18/2013 8:18:00 AM
Project:	KANAWHA WER STUDY 2 NOV 2013	Date Received:	11/19/2013
Lab ID:	1311J31-01A	Matrix:	Liquid
Client Sample ID:	2013 EQUIPMENT BLANKS	Site ID:	

Analysis	Result	MDL	PQL	MCL	Qual	Units	Date Analyzed	NELAP
METALS BY ICP-MS			Method: EPA 200.8			Analyst: JD		
Copper	0.0016	0.0010	0.0050	NA	J	mg/L	11/21/2013 5:04 PM	PAVA

By TGH on 2-7-14:
Report corrected by REIC
on 2-7-14 to show
MDL

WO#: 1311J31

Date Reported: 12/11/2013

Collection Date: 11/18/2013 8:18:00 AM
Date Received: 11/19/2013
Matrix: Liquid
Site ID:

Analysis	Result	MDL	PQL	MCL	Qual	Units	Date Analyzed	NELAP
METALS BY ICP-MS	Method: EPA 200.8						Analyst: JD	
Copper	0.0011	0.0010	0.0050	NA	J	mg/L	11/21/2013 5:10 PM	PAVA
ORGANIC CARBON, TOTAL	Method: SM5310 C-2000						Analyst: DSD	
Total Organic Carbon	0.57	0.20	1.00	NA	J	mg/L	11/22/2013 3:34 PM	PAVA

By TGH on 2-7-14:

Report corrected by REIC
on 2-7-14 to correct
analysis date of TOC